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OCT 20 1995

Montana Department of  
Environmental Quality  
Waste Management Division

Richard Knatterud, P.E.  
Hazardous Waste Program  
Waste Management Division  
Department of Environmental Quality  
PO Box 200901  
Helena, MT 59620-0901

October 20, 1995

RE: Material Management Practices  
at Asarco's East Helena Plant

Dear Mr. Knatterud:

This is in response to your August 11, 1995 letter requesting additional information about some of Asarco's material and waste management practices. Your requests are typed in bold and are followed by Asarco's responses.

1. Filter Cake

MDEQ will consider this matter resolved upon notification that the paving project in the vicinity of the HDS building, as proposed in your letter, has been completed.

As you observed in your August 29 inspection of the plant, the paving project in the vicinity of the HDS building is complete.

2. Plant Water

MDEQ will consider this matter resolved upon receipt of a letter from ASARCO indicating that the discontinuation of this practice is permanent.

Asarco certifies by this letter that it has permanently ceased the practice of using plant water for dust suppression purposes.

3. Precious Metals

No response from ASARCO is required on this issue.

4. Arsenical Dust and Cadmium Calcines

MDEQ requests further data (i.e. literature cites, personal contacts, etc.) to validate the claim that arsenical dust contributes to the arsenic necessary to the metallurgical balance between copper and arsenic.

The East Helena plant has not received or used any arsenical dust in its smelter operation since 1989.

In the smelting of complex lead concentrates containing minor elements such as arsenic, it is necessary to separate the arsenic in a separate phase early in the lead refining process. Failure to do so causes the arsenic to report to the lead bullion, from which it is more difficult to remove. At East Helena, the arsenic is removed through the formation of arsenic speiss in the dross reverb furnace. To get the speiss to form properly, a proper balance between copper and arsenic must be maintained in the feed materials. Prior to 1990, the plant operators at East Helena occasionally used arsenical dust to achieve that balance.

The need to control the copper to arsenic ratio in the lead smelting charge has been addressed in a paper by A.G. Matyas entitled "Metallurgy of lead-copper dross smelting", published in Transactions of the Institution of Mining and Metallurgy, December 1977, pp. C190-C194. Attachment 1. The paper presents results on equilibrium studies in the Pb-Cu-As-S system and discusses the implications for the smelting of lead-copper dross in the lead refining process. It emphasizes the importance of maintaining high Cu to Pb ratios in speiss and the strong relationship between the Cu:Pb ratio and the As:Cu ratio in speiss.

The synopsis of the paper states that "the Cu:Pb ratio of matte and speiss, which is the gauge of the selectivity between copper and lead, was found to be related principally to the As:Cu ratio of the speiss." The paper states further that "application of the results to industrial practice indicates that, to maximize the Cu:Pb ratio in the speiss products during copper dross smelting, it is desirable to ... limit the Cu:As ratio of the speiss within fairly narrow limits about a value of approximately 4." Also, Figure 5 in the paper illustrates clearly that below a Cu:As ratio in speiss of 2.5, the arsenic content of the lead phase shows a significant increase in arsenic, making it more difficult to refine.

#### A. Arsenic Speiss

MDEQ requests information regarding whether or not the arsenic speiss is manufactured into an arsenic product. MDEQ requests a description of how the arsenic product is used. If the arsenic is not manufactured into a product, then MDEQ requests information on what becomes of the arsenic. Include in your description quantities of arsenic that are captured.

Asarco has not manufactured arsenic speiss into an arsenic product since the closure in 1986 of its arsenic plant in Tacoma. That plant produced arsenic metal and arsenic trioxide.

Asarco currently sends the arsenic speiss from the East Helena plant to its remaining copper smelters in El Paso, Texas and Hayden, Arizona. In 1994, the plant shipped 9663 tons of speiss to the smelters with an average arsenic content of 8.15%. The speiss also contains 51% copper, 400-600 oz/ton silver and 2-4 oz/ton gold. These economically significant amounts of metal are recovered in the smelting process. In addition, the arsenic in the speiss plays an important role in the electro-refining of copper anodes produced by the smelters. A proper level of the minor elements--i.e., arsenic, antimony and bismuth--must be achieved in the electrolyte utilized in a copper refinery so that a refined copper product that meets specifications can be produced. Copper smelters owned by other companies that do not have their own source of arsenic speiss must purchase speiss to add to their feed materials to increase the ratio of As: (Sb+Bi) in their anodes. In fact, the East Helena plant sometimes sells its speiss to these companies.

The arsenic from the East Helena speiss that is sent to Asarco's copper smelters that does not end up in the copper anodes either reports to: 1) in-process materials, such as copper converter flue dust (that also contains lead) that is returned to East Helena for further metals extraction; or 2) primary copper smelting slag, which is a Bevill waste.

#### B. Baghouse Dust

MDEQ requests information regarding how and where the cadmium dust is processed and whether it is processed as a waste or as a product. Include in your description quantities of cadmium that are processed.

High cadmium blast furnace baghouse dust (17% or more cadmium) from the East Helena plant is an in-process material that is sent to Encycle in Corpus Christi, Texas to recover cadmium and zinc. The dust is shipped in covered gondola railcars. Upon arrival, it is mixed with water to create a slurry. The slurry is then placed into a reaction tank where sulfuric acid is used to leach out the cadmium and zinc. Insoluble lead sulfate remains behind and is recovered as a filter cake that is returned to the East Helena plant for further lead extraction. The cadmium-rich filtrate is then handled in one of two procedures.

The preferred procedure involves routing the filtrate from the first reaction tank to a second reaction tank to which zinc dust is added to precipitate the cadmium from the leach solution. The high purity cadmium pellets formed in this reaction are filtered to produce a cadmium sponge. The zinc sulfate that is formed is treated with caustic soda to recover zinc as a hydroxide. The cadmium sponge and zinc hydroxide are then sold to primary smelters for recovery of the cadmium and zinc.

The second procedure involves routing the cadmium-rich filtrate from the acid leaching process into a separate reaction tank where it is treated with soda ash to form a cadmium/zinc carbonate product. The product is sold to primary smelters for metal recovery.

The cadmium produced through both of the procedures is used world-wide in the production of nickel-cadmium batteries and in the manufacture of electronic components.

In 1994, the plant shipped 1837 tons of high cadmium baghouse dust to Encycle with an average cadmium content of 19.5%.

## 5. Materials from TSDFs

### A. Sweeps from Drew Resources

MDEQ requests a more detailed description on what these sweeps are, such as their physical state, whether they originated from processing of spent materials, whether the sweeps contain "toxic organics along for the ride," etc. ASARCO also needs to state that the sweeps are a characteristic by-product as opposed to a listed by-product.

Drew Resources (a subsidiary of Safety-Kleen) is in the business of recovering silver and gold from characteristic byproducts of the photographic industry. The "sweeps" sent to the East Helena Plant are primary products of Drew Resources, do not originate from the processing of spent material, and do not contain "toxic organics along for the ride". Drew recovers silver from photo processing solutions by precipitating the silver onto steel wool. The steel wool is then ground, screened and shipped for smelting to the East Helena plant. Drew also recovers silver from the ash produced by the incineration of photographic materials. The ash is basically the metals that remain after any organic matter has been removed by incineration. Drew grinds and screens the material before sending it to East Helena for smelting. The materials Drew sends to East Helena for smelting are sometimes referred to as "sweeps" because they are fine in size and in the form of a powder. The sweeps from Drew Resources are very high in silver content (1,000-3,000 oz./ton). They are used at the East Helena plant as substitutes for ores or concentrates.

### B. Residue from Encycle

MDEQ requests a more detailed description on what these residues are, i.e. their physical state, whether they originated from processing of spent materials, etc.

Encycle recycles hazardous (listed and characteristic) and non-hazardous metal bearing wastes, as well as non-waste metal bearing materials. Encycle's recycling process produces products

that are sent to smelters. The smelters use Encycle's products as effective substitutes for commercial products, like ore concentrates.

Encycle sends "lead product" material to the East Helena plant. This has apparently been referred to as "residue" material on the bill of lading shipping papers. However, this description is not accurate. The material is produced intentionally for sale to the smelter and is not considered a residual material in Encycle's process, but rather as the primary product.

The physical characteristics of the lead product produced by Encycle resemble those of a lead concentrate in terms of particle size, handling characteristics and lead content--i.e., an average of 28.3% Pb in 1994.

The Texas Natural Resource Conservation Commission has made a determination that the lead bearing material produced by Encycle is a product, not a solid waste. (Attachment 2). The product is used at East Helena as a substitute for a commercial product: lead concentrates.

#### 6. CRT/TV Tubes

MDEQ requests that ASARCO revisit this issue and provide a response that does not rely on EPA's letter.

The April 1992 letter from Region IX EPA determined that the CRT/TV tubes were exempt from regulation as a hazardous waste under 40 CFR § 261.2(e)(1), which is the federal counterpart to ARM 16.44.302(5)(a)(i). Section 261.2(e)(1) exempts materials from regulation if they are being:

used or reused as ingredients in an industrial process to make a product, provided the materials are not being reclaimed.

While Asarco properly relied on EPA's interpretation of its own regulations in accepting the CRT/TV tubes for smelting, there are two other regulatory provisions under which the tubes would also be exempt from regulation under the hazardous waste rules.

The first provision is found in ARM 16.44.302(5)(a)(ii). (5)(a)(ii) exempts materials from regulation if they are being:

used or reused as effective substitutes for commercial products.

As Asarco explained in its June 7 letter, the tubes, which are 54% silica by weight, are used as a substitute for silica flux that Asarco would otherwise have to procure from commercial suppliers. The silica in the tubes is not recovered in the

smelting process; rather, it acts as a flux that collects unwanted portions of the ores and concentrates that are being processed. Asarco's use of the tubes as a substitute for silica flux is thus clearly exempt from regulation under the hazardous waste rules.

In your March 8 letter, you expressed concern about the fact that some lead is recovered from the tubes. While any recovery of lead is incidental to the primary purpose for which the tubes are being used, the fact that some lead is recovered does not make the exemption in (5)(a)(ii) inapplicable. In the first place, unlike its companion provision in (5)(a)(i), there is no proviso about reclamation attached to (5)(a)(ii). By its plain terms, the exemption applies whether or not the substitute materials are being reclaimed. Moreover, EPA has expressly stated that it does not consider the use of substitutes "in processes [like primary smelting] that normally use raw materials as principal feedstocks" as a form of reclamation. When EPA first proposed the federal counterpart to (5)(a)(ii), it stated:

the [effective substitute] exception does include those situations where material values are recovered from these substitute materials. Examples are sludges or spent materials used as substitutes for ore concentrates in primary smelting. The Agency does not believe these processes constitute reclamation, in spite of the recovery or regeneration step, because the materials are literally being used as alternative feedstocks.

48 Fed. Reg. 14488 [emphasis supplied]. Thus, it is clear that even if the tubes were processed by Asarco solely for the purpose of recovering their lead value, the exemption in (5)(a)(ii) would still apply. The tubes would simply be acting as substitutes for the ore concentrates normally used as feedstocks in Asarco's primary smelting operation.

Finally, Asarco's processing of the tubes would be exempt from regulation even if the recovery of lead from the tubes were considered a form of reclamation. Under ARM 16.44.302(3)(c), only listed sludges, listed byproducts and spent materials that are being reclaimed are subject to regulation. Characteristic secondary materials, like the tubes, that are being reclaimed are exempt from regulation.

## 7. Other Issues

### A. Street Sweepings

ASARCO must provide a response that includes an explanation as to the present disposition of the sweepings that correlate to the test data in Attachment 1. The response should include a

plant for the removal of the sweepings in the vicinity of the affected area.

Contrary to MDEQ's understanding, the street sweepings that Asarco placed in the fields east of the smelter in September 1994 were placed there "under the guidance of the Federal Superfund Program." Their placement may not therefore be considered a violation of the Montana Hazardous Waste and Underground Storage Tank Act.

Asarco and EPA entered into an Administrative Order on Consent for Removal Action ("AOC") in 1991 in connection with the CERCLA cleanup of its East Helena Plant. The AOC requires Asarco to remove contaminated residential soil from the City of East Helena. Asarco stored the soil removed during 1991 and 1992 in a containment area just east of the East Helena plant. However, following EPA's approval of a feasibility study by Asarco, Asarco began hauling the soil directly to the east fields where it was initially blended into existing soil and where it is now placed directly on the east fields.

During the excavation and hauling of the soil to the east fields, some of the soil inadvertently spilled on roadways in the City of East Helena. Both the citizens and EPA expressed concern about the spilled soil and, consequently, EPA required Asarco to sweep it up. The road sweeping, which will continue until the soil removal project is complete, is done by Asarco's contractor, Hydrometrics, with a Tennant sweeper.

Hydrometrics dumps the sweepings it collects in the east fields with the other residential soil that has been removed from the City of East Helena. As the sweepings and the other residential soil come from the same source, no effort is made to segregate them.

Asarco obtained the September 1994 samples referred to in MDEQ's letter from the Tennant sweeper used by Hydrometrics to sweep up spilled residential soil pursuant to CERCLA. Asarco took the samples to assist it in evaluating what to do with the road sweepings that it was then planning to collect pursuant to its lead SIP. The lead SIP requires Asarco to regularly sweep all of the roadways in the City of East Helena, not just the roads where residential soil may have been spilled, to reduce the amount of lead-bearing fugitive dust to which the citizens might be exposed. Asarco initiated the lead SIP street sweeping program in March 1995. With MDEQ's approval, Asarco is depositing the street sweepings from the lead SIP program in its ore storage and handling building from whence they will be recycled to recover their metal values.

B. Materials from Lantz Lenses

ASARCO must describe how each of these wastes, including the pitch, fits into the hazardous waste and/or recycling regulations.

Asarco receives byproducts of the optical lens manufacturing business from Lantz Lenses. Until May 1995, the byproducts consisted exclusively of wet grindings. In May, Lantz sought approval from the Minnesota Pollution Control Agency to add certain additional "lead-contained waste" to the wet grindings for recycling purposes. The Agency approved the additional materials as byproducts, provided that Lantz got approval from Montana before shipping them to Asarco. Lantz contacted Tom Hallberg with MDEQ and received such approval. As a consequence, the byproducts from Lantz are made up of wet grindings, which make up over 97% of the material received, and small amounts of defective glass pieces, sweepings from around the workbenches and glass pieces with some pitch binder attached. Asarco uses the byproducts as a substitute for silica flux and also recovers some lead from them.

The regulatory status of each of the byproducts, including the pitch, is the same as described in Question 6 above for the CRT/TV tubes. The glass pieces to which some pitch binder is attached, which is only a trivial amount of material--i.e., less than 1% of the materials received from Lantz and less than 0.00048% of the material smelted at the plant each year--are not burned for energy recovery. The blast furnace is fired by the burning of foundry coke.

Please let me know if additional information or explanation is needed to satisfy your concerns.

Sincerely,

  
Robert A. Little

cc: Robert Comer  
Richard Marcus  
Jon Nickel  
Larry Jensen  
Krishna Parameswaran  
Glendon Archer



## ATTACHMENT 1

Metallurgy of Lead-Copper Dross Smelting Paper

# Metallurgy of lead-copper dross smelting

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## Synopsis

A more comprehensive understanding of industrial copper dross smelting metallurgy has been provided by a study of equilibria in the system  $Pb-Cu-As-S$  and of the effects of antimony and sodium sulphide on these equilibria. The  $Cu : Pb$  ratio of matte and speiss, which is a gauge of the selectivity of the separation between copper and lead, was found to be related principally to the  $As : Cu$  ratio of the speiss. The effect of antimony in the speiss was similar to, but not as large as, that of arsenic. The addition of sodium sulphide to the matte was found to enhance the  $Cu : Pb$  ratio of both matte and speiss, and to reduce the  $As$  content of the matte, as well as the dissolved  $Cu$ ,  $As$ , and  $S$  contents of the metallic lead phase. Application of the results to industrial practice indicates that, to maximize the  $Cu : Pb$  ratio of the matte and speiss products during copper dross smelting, it is desirable to (a) limit the  $Cu : As$  ratio of the speiss within fairly narrow limits about a value of approximately 4; (b) maintain sufficient additions of soda ash or sodium sulphide; and (c) maintain the speiss layer in the dross smelting furnace at a temperature only slightly above that of its liquidus.

The recovery of copper from blast-furnace lead bullion poses a significant industrial problem because of the relatively poor selectivity generally obtainable during copper dross smelting. Thus, the  $Cu : Pb$  ratio in the by-product matte and/or speiss is rarely in excess of about 6. The chemistry of copper dressing is fairly well established;<sup>1</sup> but the metallurgy of the subsequent smelting of the dross has been investigated only to a limited extent. The equilibria between lead and  $Cu_2S-PbS-Na_2S$  mattes were studied by Kuxmann and Steinkamm,<sup>2</sup> and lead-matte equilibria pertinent to the metallurgy of continuous copper dressing to matte were analysed by Moffatt and Willis.<sup>3</sup> There is a lack of information, however, about the role of arsenic in copper dross smelting. As shown in Table 1, arsenic is a common component of industrial copper drosses and accounts for the production of a significant proportion of the copper as speiss. Previous investigations on the effect of arsenic have been limited to lead-speiss systems<sup>4,5</sup> in the absence of matte.

To provide a more comprehensive understanding of industrial copper dross smelting metallurgy equilibria in the system  $Pb-Cu-As-S$  and the effect of antimony and sodium sulphide on these equilibria were studied experimentally in the present investigation.

## Experimental

A stock speiss which was analysed as 31.6%  $As$  and 63.4%  $Cu$  was prepared by the addition of metallic arsenic to a melt of electrolytic copper at  $1150^\circ C$ . The  $As : Cu$  ratio of this speiss was chosen at 0.5,

as of copper matte to the range of industrial compositions studied. A stock matte, which was analysed as 54.7%  $Cu$  and 24.6%  $Pb$  (typical of industrial practice), was prepared by the addition of reagent-grade  $PbS$  to a melt of  $Cu_2S$  at  $1150^\circ C$ .

The apparatus used for the equilibrium experiments had been described previously.<sup>5</sup> In each test 12 g of pure metallic lead, 12 g of speiss and 12 g of matte were charged to an alumina crucible (internal diameter, 22 mm, height, 33 mm). The  $As : Cu$  ratio of the speiss was varied by the addition of a predetermined amount of metallic copper or arsenic. In some tests the charge was doped with antimony, and in others with reagent-grade  $Na_2S$ .

Equilibrations of duration 3, 6 and 9 h were carried out at 1000 and  $1150^\circ C$  (typical industrial matte-forming temperatures) under a nitrogen atmosphere. At the end of the equilibration time the reaction tube, which contained the crucible, was removed from the furnace and quenched from the outside with an air blower. The solidified lead, speiss and matte phases separated readily from one another and from the alumina crucible.

Table 1 Industrial copper dross smelting data\*

Smelter	Product	Analysis, %			
		Cu	Pb	As	Sb
El Paso <sup>6</sup>	Dross	25	59	4.6	1.7
	Matte	47	9	1.9	0.7
	Speiss	68	8	15	2.2
Port Pirie <sup>7</sup>	Dross	15	68	2.5	0.7
	Matte	40	9	0.5	0.1
	Speiss	61	9	16	4.8
La Oroya <sup>10</sup>	Dross	22	59	6.4	2.3
	Matte	34	10	2.8	0.9
	Speiss	58	12	19	5.1
East Helena <sup>11</sup>	Dross	20	58	3.0	3.5
	Matte	46	10	0.8	0.3
	Speiss	60	10	18	6.6
Brunswick <sup>12</sup>	Dross	20	60	7.5	0.5
	Matte	40	25	3.0	0.4
	Speiss	50	20	23	5.5

\* Dross smelted in bottom-cooled reverberatory furnace with additions of 3-8% soda ash and 2% coke fines by weight of dross.

† Copper dross smelting operation discontinued in 1962.

The lead button was sampled by drilling, and the matte and speiss were ground to -100 mesh for chemical analysis. All analyses were made by atomic absorption spectroscopy.

## Results and discussion

The experimental results are summarized in Table 2. From a material balance (not reported) on the various elements it was found that 20-30% of the arsenic, 15-30% of the sulphur and 5-10% of the lead volatilized. The loss of these elements appeared to be independent of the time of equilibration, and the product analyses were similar after 3, 6 and 9 h (Table 2); therefore a 3-h equilibration period was chosen for most of the

Test number*	As : Cu ratio of speiss	Experimental conditions†	Phase	Cu	Pb	As	Sb	Nb	S
4	0.097	1000°C	Matte	63.5	10.2	0.50	—	—	—
			Speiss	46.2	42.0	4.43	—	—	—
			Lead	17.4	—	0.96	—	—	1.2
2	0.22	1000°C	Matte	64.0	13.2	—	—	—	—
			Speiss	55.5	26.4	12.0	—	—	—
			Lead	8.52	—	1.27	—	—	0.70
5	0.22	1000°C	Matte	63.5	14.9	2.68	—	—	—
			Speiss	55.8	25.8	12.3	—	—	—
			Lead	11.8	—	1.83	—	—	0.82
11	0.29	1000°C	Matte	61.0	19.0	—	—	—	—
			Speiss	60.2	18.2	17.6	—	—	—
			Lead	3.06	—	1.07	—	—	0.19
1	0.36	1000°C	Matte	55.0	22.2	3.19	—	—	—
			Speiss	57.8	13.7	20.8	—	—	—
			Lead	2.66	—	1.47	—	—	0.37
3	0.36	1000°C Equilibration, 6 h	Matte	54.3	22.4	—	—	—	—
			Speiss	58.8	15.3	20.8	—	—	—
			Lead	4.20	—	2.06	—	—	0.39
8	0.36	1000°C Equilibration, 9 h	Matte	54.5	22.4	—	—	—	—
			Speiss	58.7	15.9	21.3	—	—	—
			Lead	1.79	—	1.17	—	—	0.18
17	0.39	1000°C	Matte	51.7	28.2	3.18	—	—	—
			Speiss	53.6	22.2	20.8	—	—	—
			Lead	3.17	—	2.71	—	—	0.52
16	0.50	1000°C	Matte	45.4	33.8	3.51	—	—	—
			Speiss	41.9	33.6	20.8	—	—	—
			Lead	7.98	—	6.34	—	—	1.26
15	0.13	1150°C	Matte	66.6	13.0	1.28	—	—	—
			Speiss	52.1	37.0	6.88	—	—	—
			Lead	13.3	—	1.09	—	—	0.55
6	0.22	1150°C	Matte	64.2	12.2	2.40	—	—	—
			Speiss	55.5	22.3	12.2	—	—	—
			Lead	7.69	—	1.11	—	—	0.40
14	0.36	1150°C	Matte	55.0	22.8	3.26	—	—	—
			Speiss	59.6	15.4	21.2	—	—	—
			Lead	3.37	—	1.50	—	—	0.19
13	0.13	1000°C Speiss doped with Sb	Matte	64.6	13.8	—	—	—	—
			Speiss	47.0	33.7	6.15	6.90	—	—
			Lead	9.64	—	0.78	1.35	—	0.24
7	0.18	1000°C Speiss doped with Sb	Matte	60.1	14.3	—	—	—	—
			Speiss	52.0	18.7	9.36	5.15	—	—
			Lead	3.28	—	0.58	1.20	—	0.30
12	0.36	1000°C Speiss doped with Sb	Matte	51.5	26.1	—	—	—	—
			Speiss	50.6	20.9	18.1	5.50	—	—
			Lead	3.45	—	2.10	0.64	—	0.24
19	0.16	1000°C Matte doped with Na <sub>2</sub> S	Matte	59.4	4.25	0.73	—	9.16	—
			Speiss	67.7	16.6	10.9	—	—	—
			Lead	8.82	—	0.42	—	—	0.10
18	0.41	1000°C Matte doped with Na <sub>2</sub> S	Matte	51.1	13.0	0.74	—	9.24	—
			Speiss	58.4	16.8	23.5	—	—	—
			Lead	1.74	—	1.74	—	—	0.07
20	0.53	1000°C Matte doped with Na <sub>2</sub> S	Matte	47.6	19.2	0.61	—	9.04	—
			Speiss	42.4	31.3	22.5	—	—	—
			Lead	3.48	—	6.54	—	—	0.23

\* Listed in order of increasing As : Cu ratio of speiss for each set of experimental conditions.

† Equilibration period 3 h except where otherwise noted.

## MATTE

The most industrially significant characteristic of the matte phase is its Cu : Pb ratio. This was found to be principally related to the As : Cu ratio of the speiss in both the laboratory and industrial mattes (Fig. 1). At a given As : Cu ratio in speiss, however, the industrial mattes had a somewhat higher Cu : Pb ratio than the laboratory mattes. To explain this difference the matte was doped with sodium and antimony, to simulate industrial conditions more closely.

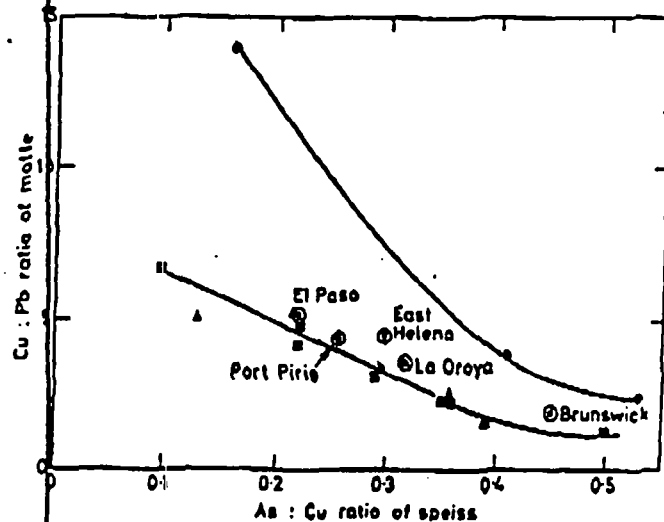


Fig. 1 Cu : Pb ratio in matte as function of As : Cu ratio in speiss: ■ 1000°C; ▲ 1150°C; ● 9% Na in matte, 1000°C; ○ Industrial data

There are no data in the literature on the sodium contents of industrial mattes, but previous investigations<sup>2,7</sup> have shown that sodium sulphide enhances the Cu : Pb ratio of matte. In the experiments reported here sufficient reagent-grade Na<sub>2</sub>S was added to ensure that after equilibration the matte contained about 9% Na (Table 2). The Cu : Pb ratios of these mattes (Fig. 1) confirm the beneficial effect of sodium.

An increase in temperature from 1000 to 1150°C was found to have no effect on the Cu : Pb ratio of the matte (Fig. 1).

To examine the effect of antimony, reagent-grade metallic Sb was added so that after equilibration the speiss contained 5–6% Sb (Table 2) – typical of industrial speisses (Table 1).

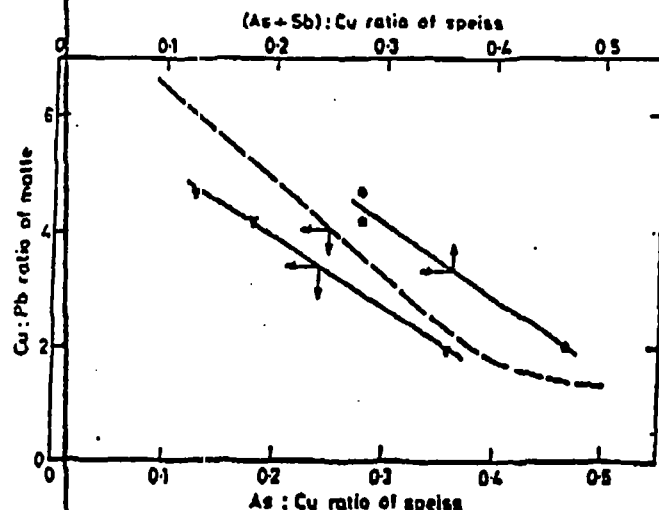


Fig. 2 Effect of antimony in speiss on Cu : Pb ratio in matte: ▼ As : Cu ratio on abscissa; ● (As + Sb) : Cu ratio on abscissa; dotted line, Na-free system from Fig. 1

plotted as a function of the (As + Sb) : Cu ratio of the speiss, it results in inconsistently high Cu : Pb ratios in the matte (Fig. 2), which indicates that the effect of antimony is not as large as that of arsenic.

The solubility of arsenic in matte was found to increase with the As : Cu ratio of the speiss as expected (Fig. 3), but was not affected by temperature in the range 1000–1150°C. The presence of sodium lowered the As solubility in matte substantially (Fig. 3), and may explain the low As levels reported for some industrial mattes.

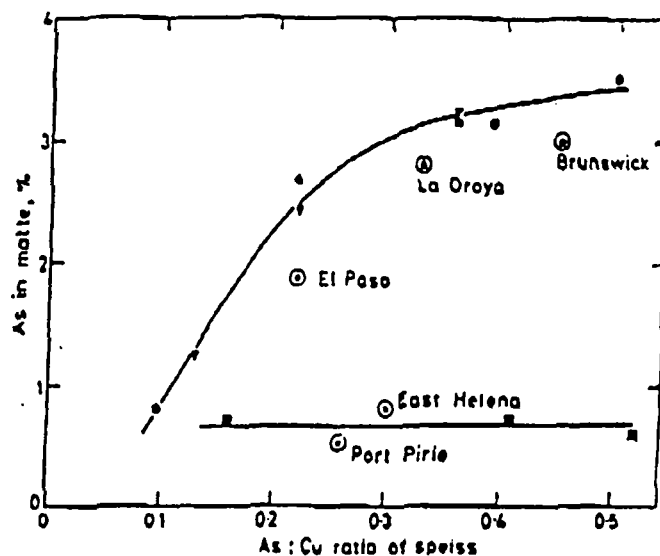


Fig. 3 Solubility of arsenic in matte as function of As : Cu ratio in speiss: ● 1000°C; ▼ 1150°C; ■ 9% Na in matte, 1000°C; ○ Industrial data

In conclusion, it appears that the Cu : Pb ratio of matte and the As : Cu ratio of the speiss with which it is in contact are strongly related, and that the Cu : Pb ratio of the matte is increased by the presence of sodium sulphide.

## SPEISS

The most significant characteristic of speiss, like matte, is its Cu : Pb ratio. This is shown as a function of the speiss As : Cu ratio in Fig. 4, in which data from the present study are compared with industrial data and with the measurements of Dice and co-workers<sup>4</sup> in the temperature range 700–800°C. The main facts shown by the curves are listed below.

- (1) The Cu : Pb ratio of speiss is also related to its As : Cu ratio; but the curve has a maximum that, unlike that of matte, shifts from a speiss As : Cu ratio of about 0.25 to 0.35 as the temperature increases from 700 to 1000°C.
- (2) An increase in temperature from 700 to 1000°C has a profound effect on the Cu : Pb ratio of the speiss, owing principally to the increased solubility of lead (Table 2).
- (3) The presence of sodium in the matte in contact with the speiss increases the Cu : Pb ratio of the speiss.

In industrial practice copper dross is smelted in a bottom-cooled reverberatory furnace,<sup>8</sup> which enables speiss to be tapped at a lower temperature than the matte phase above it. This is reflected in the Cu : Pb ratios of industrial speisses (Fig. 4); the presence of sodium in the industrial

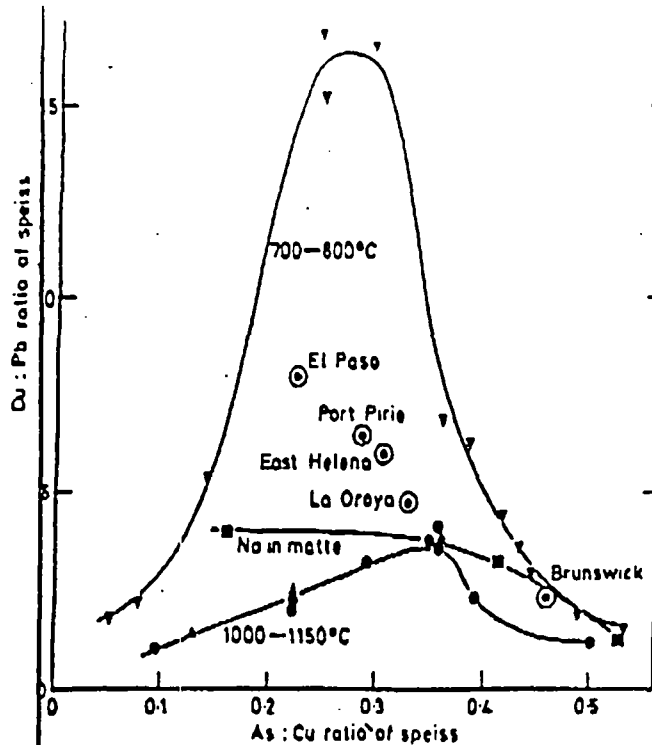


Fig. 4. Cu : Pb ratio in speiss as function of As : Cu ratio:  
 ● 1000°C; ▲ 1150°C; ■ 9% Na in matte, 1000°C; ▼ 700-800°C;  
 ○ Industrial data

to have only a secondary effect compared to that of temperature.

These results may also explain why the addition of scrap iron to a dross furnace which produces speiss of high As : Cu ratio has been reported to increase the Cu : Pb ratio of the speiss.<sup>13</sup> This was believed to result from an increase in bath fluidity<sup>13,14</sup> with the formation of  $Fe_3As$ , but the present data suggest that a more likely reason was an enhancement of the activity coefficient of copper in the speiss in the presence of iron.

#### LEAD

The dissolved copper, arsenic and sulphur contents of the lead phase are shown as a function of the As : Cu ratio of the speiss in Fig. 5. The shapes of the curves for Cu and As are consistent with previous investigations,<sup>4,5</sup> and the data illustrate the substantial effect of temperature on the solubilities of these elements in lead. Lead is tapped from the copper dross smelting furnace at a temperature usually below 500°C, and is therefore much lower in Cu, As and S content than the values obtained in the present experiments.

The data also clearly show the effect of sodium in the suppression of the solubilities of Cu, As, and S in lead; furthermore, the similarity in the shapes of the curves for copper and sulphur (but not for arsenic) is indicative of the much higher affinity of copper for sulphur than for arsenic.

#### Application to Industrial practice

The results of this investigation allow certain conclusions to be drawn with regard to industrial copper dross smelting practice. As the objective of smelting copper dross is to concentrate copper in a form suitable for further treatment, and to reject lead from the dross, it is desirable to maximize the Cu : Pb ratio of the matte and speiss produced. The Cu : Pb ratio of matte is directly related to the

combined matte-speiss product depends on the relative proportions of matte and speiss produced. For smelters that produce an arsenic-lean dross (less than, say, 3% As), a relatively small amount of speiss will be obtained, and the objective should be to maximize the Cu : As ratio of this speiss — for example, by enrichment of the copper content of the smelter feed. For smelters where the dross is richer in arsenic, and where, therefore, proportionately greater amounts of speiss are produced, it is desirable to maintain the Cu : As ratio of the speiss within fairly narrow limits around a value of about 4, by adjustment of the Cu : As ratio of the dross. This can be accomplished by the addition of copper-bearing materials to the blast-furnace, or by the selective elimination of arsenic — for instance, by incorporation of scrap iron in the blast-furnace charge. Similar considerations with regard to speiss composition apply if the matte and speiss are produced directly in the lead blast-furnace, as at the Hoboken smelter.<sup>15</sup>

The Cu : Pb ratio of both matte and speiss is enhanced by the presence of sodium in the matte; furthermore, the recirculation of copper and arsenic to the lead refining kettles is reduced with the presence of sodium in the matte. Soda-ash additions should therefore be maintained at levels just below slagging of the sodium. In the case of low-sulphur drosses, the use of a sodium sulphide reagent is equally beneficial.<sup>16</sup>

Finally, because of the profound effect of temperature on the Cu : Pb ratio of speiss, it is

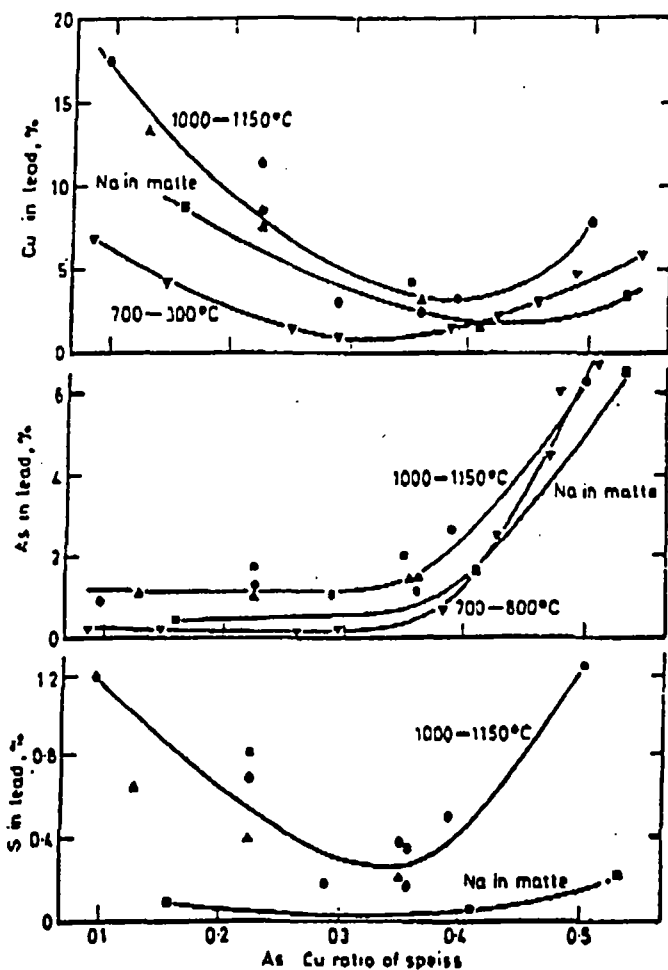


Fig. 5. Lead composition as function of As : Cu ratio in speiss:  
 ● 1000°C; ▲ 1150°C; ■ 9% Na in matte, 1000°C; ▼ 700-800°C

the speiss feasible with a thick speiss layer in the cross reverberatory furnace and if the speiss taphole is located well below the matte taphole, away from the burner-end, in the coolest part of the furnace.<sup>8</sup>

## Conclusions

The measurement of equilibria in the system Pb-Cu-As-S and the effect of antimony and sodium sulphide on these equilibria have provided a more comprehensive understanding of copper dross-smelting metallurgy. The principal factor that governs the selectivity of the separation between copper and lead during dross smelting was found to be the Cu : As ratio of the speiss phase: thus, the Cu : Pb ratio of the matte phase was proportional to the Cu : As ratio of the speiss, and the Cu : Pb ratio of the speiss reached a maximum of about 4 at a Cu : As ratio of about 3 in the temperature range 1000–1150°C. Temperature had a substantial effect on the solubility of lead in speiss, and at a temperature of 700–800°C the maximum speiss Cu : Pb ratio increased to about 15. The effect of antimony in the speiss was similar to, but not as large as, that of arsenic. The addition of sodium sulphide to the matte enhanced the Cu : Pb ratio of the matte (in agreement with previous laboratory and industrial data) and speiss, and reduced the dissolved Cu, As and S contents of the lead phase. The latter factor is important in industrial practice, as it implies a reduced recirculation of these elements to the lead-refining kettles. Other conclusions that arise from this work are that, in copper dross smelting practice, the Cu : As ratio of the speiss should be maintained within prescribed limits, sufficient sodium-bearing reagents should be added during dross smelting, and a thick cool speiss layer should be maintained in the dross furnace.

## Acknowledgement

The author is indebted to S. Tanner, who suggested that arsenic played a key role in copper dross smelting; to M. Thibodeau, who carried out the experimental work; and to Dr. P. Tarassoff, for his suggestions in the preparation of the paper. Permission by Noranda Mines, Ltd., to publish the work is gratefully acknowledged.

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## ATTACHMENT 2

Texas National Resource Conservation Commission Determination

## TEXAS WATER COMMISSION

B. J. Wynne, III, Chairman  
Paul Hopkins, Commissioner  
John O. Houchins, Commissioner



September 27, 1989

Allen Beinke, Executive Director  
Michael E. Field, General Counsel  
Brenda W. Foster, Chief Clerk

RECEIVED

SEP 29 1989

MANAGER'S OFFICE  
CORPUS CHRISTI PLANT

R. T. Cardenas  
Encycle/Texas, Inc.  
Post Office Box 4767  
Corpus Christi, Texas 78469-4767

Re: Solid Waste Registration Number 30003

Dear Mr. Cardenas:

This is in response to your letter of July 12, 1989 to the Texas Water Commission (TWC), in which you requested concurrence that the described solids, generated at Encycle/Texas, Inc., are not solid waste when sent to a smelter for the production of refined metals.

The specific exclusion from the definition of a solid waste cited in your letter corresponds to 31 Texas Administrative Code (TAC) 335.1(Solid Waste Definition)(F)(ii). This provision states that materials which are "used or reused as effective substitutes for commercial products" are not considered solid waste, provided they are not disqualified under 31 TAC 335.1(Solid Waste Definition)(G) for this exemption.

The information submitted in your letter of July 12th, Keith Hopson's letter of October 7, 1988 and the July 14, 1989 meeting between representatives of Encycle/Texas Inc. and the TWC, indicates that Encycle/Texas, Inc.'s solids contain higher concentrations of salable metals than typically found in metal concentrates generated from raw ore. It is the understanding of the TWC that the portion of the solids, which will not become refined metal, does not interfere with normal smelting operation or contain hazardous constituents other than: 1) metals which will be "refined" and/or 2) constituents which could cause the material to exhibit a characteristic of a hazardous waste. TWC staff also understands that the solids will be sent to a primary smelting operation. Based upon this information, it appears to the TWC that



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the solids are effective substitutes for the metal concentrates these smelters ordinarily accept. Due to the fact that ore concentrates are products produced from raw ore and are managed as commodities, TWC believes that your solids are eligible for the exclusion from the definition of a solid waste provided to materials which are "used or reused as effective substitutes for commercial products."

TWC staff would like to remind you that it is Encycle/Texas, Inc.'s continuing obligation, under 31 TAC 335.1(Solid Waste)(H), to be able to provide sufficient information to demonstrate that they meet the terms of the exclusion and that the exclusion is not nullified under 31 TAC 335.1(Solid Waste)(G). TWC suggests that, at a minimum, records be kept which reflect the following:

1. The quantity of solids generated;
2. The description (including composition) and quantity of solids sent to each smelter;
3. The identity of each smelter;
4. The quantity of precipitated solids introduced into each smelter's operation; and
5. A description of products produced and their disposition.

The above list is presented to you for guidance purposes only and is not intended to serve as a complete listing of information that might be required to demonstrate that the solids are being managed in accordance with all applicable regulations which may be in effect at the time the appropriateness of the exclusion may be questioned.

If there is a change in the management of the solids (including, but not limited to, the process into which it is incorporated), Encycle/Texas, Inc. shall immediately notify the TWC, in writing, of those changes. If the solids must be disposed of, they will be considered an industrial solid waste and subject to all applicable regulations of 31 TAC Chapter 335 (including, but not limited to, manifesting requirements).

In subsequent telephone conversations between Mr. Hopson and members of the TWC, as well as Mr. Hopson's letter of August 7, 1989 to Lisa Montgomery of the TWC, it was requested that the TWC concur with the following conclusions:

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- 1) Encycle/Texas, Inc. solids are not waste when used as ore concentrates in operations other than primary smelting;
- 2) Solids, which are similar to Encycle/Texas, Inc. solids, but are generated by another facility and then sent to Encycle/Texas, Inc. for further treatment and/or sale, are not considered waste when managed as Encycle/Texas, Inc. solids which have been excluded from regulation; and
- 3) Encycle/Texas, Inc. solids, other than those substituting for ore concentrates, are not solid waste if they are effectively used as substitutes for commercial products or as ingredients in industrial processes.

In evaluating these subsequent requests, TWC staff would like to note that each request for an exclusion from regulation as a solid waste is centered around not only the material in question, but also the use of that material.

In order to evaluate your conclusion that the solids are not waste when used as ore concentrates in operations other than primary smelting, TWC staff requires, at a minimum, the following information:

- 1) Identification of the types of operations;
- 2) A description of these operations; and
- 3) A comparison of the solids and the ore concentrate typically used in this type of operation.

The comparison of the solids and the ore concentrate it will be replacing should include, but is not limited to, the identity and concentration of toxic constituents and potentially harmful substances not normally found in the ore concentrate and the identity and concentration of toxic constituents and potentially hazardous substances which exceed levels normally found in ore concentrates.

If the solids are substituting for ore concentrates typically used in these specific operations, and the solids do not contain concentrations of toxic constituents and/or potentially harmful substances which exceed those normally found in these types of ore concentrates, and the solids and their management are in compliance with the regulations exempting a material from the definition of a solid waste, then the solids used as ore concentrates in operations other than primary smelting operations, would not be considered waste.

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TWC has reviewed your conclusion that solids, which are similar to Encycle/Texas, Inc. solids, but are generated by another facility and then sent to Encycle/Texas, Inc. for further treatment and/or sale, are not considered waste when managed as Encycle/Texas, Inc. solids which have been excluded from regulation. TWC would like to state that the fact that a portion of the described process is performed at another location does not alter the status of Encycle/Texas, Inc.'s solids, unless the off-site processing results in solids which differ in composition and characteristics from those produced solely at Encycle/Texas, Inc.

TWC staff has reviewed the conclusion that the solids, other than those substituting for ore concentrates, are not solid waste if they are effectively used as substitutes for commercial products or as ingredients in industrial processes. TWC has adopted legislation which provides for these particular type of exclusions. (Please review 31 TAC 335.1(Solid Waste Definition)(F)(i) and (ii)). A material managed under these circumstances would not be considered a solid waste unless it was managed as described at 31 TAC 335.1 (Solid Waste Definition)(G).

If you wish to have TWC staff review a particular use of your solids in accordance with one the above listed exclusions, please provide the following information, in writing, to the Waste Classification Unit:

1. Evidence showing that the solids can actually be recycled and in sufficient quantities to qualify for the exemption;
2. A detailed description of the industrial process in which the solids will be used and how they will be used in that process;
3. Verification that the solids are handled in a safe and acceptable manner;
4. The effectiveness of the solids in comparison to the material they will be replacing;
5. The concentration of the constituents in the solids that are needed to obtain the proposed results and the basis for this determination;
6. The criteria the solids must meet before they can be accepted for the proposed recycling activity, the basis for this criteria, and the type of procedures to be

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followed to ensure the solids meet acceptance criteria (including quality assurance/quality control procedures);

7. The material value the solids contribute to the recycling activity; and
8. The identity and concentration of toxic and/or potentially harmful constituents in the waste and what these constituents contribute to the recycling activity.

While it is the policy of TWC to promote the reuse and recycling of waste, exclusion from regulation is not automatic for all recyclable materials. In order to exempt any waste from regulation as solid waste, TWC must be assured that the method of managing and recycling the waste is legitimate, beneficial, allowable under current state and federal regulations, and assures the protection of the public health and the environment.

Sincerely,



Allen P. Beinke  
Executive Director

cc: Texas Water Commission District 12 Office - Corpus Christi